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(21) International Application Number: PCT/US95/04698 (22) International Filing Date: 18 April 1995 (18.04.95) (30) Priority Data: 08/230,026 19 April 1994 (19.04.94) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: LOGOTHETIS, Anestis, Leonidas; 2816 Kennedy Road, Wilmington, DE 19810-3430 (US). (74) Agents: SIEGELL, Barbara, C. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: BR, CN, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PERFLUOROELASTOMER CURING (57) Abstract Nitrile containing perfluoroelastomers are cured by a combination of a peroxide, a coagent, and a catalyst which causes crosslinks to form using the nitrile groups. The method is relatively fast and economical, and gives vulcanizates which have excellent high temperature properties. Triphenyltin hydroxide is an exceptionally good catalyst for the formation of crosslinks from nitrile groups in perfluoroelastomers.		

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TITLE

PERFLUOROELASTOMER CURING

FIELD OF THE INVENTION

Disclosed herein is a composition and method for
5 the curing (crosslinking) of a perfluoroelastomer
containing nitrile groups using a dual cure system of a
peroxide catalyzed cure and a catalyst that crosslinks
using the nitrile groups. The cure requires only a
short time in a mold, and produces a vulcanizate that
10 has thermally stable crosslinks.

TECHNICAL BACKGROUND

Perfluoroelastomers are materials often possessing
very good resistance to high temperatures and/or
chemical attack. This makes them valuable for uses such
15 as O-rings and gaskets where high temperatures and/or
chemicals are present, and good sealing properties are
needed. One drawback to the use of these materials is
their cost, which is often contributed to by the high
cost of molding and curing (crosslinking)
20 perfluoroelastomer parts. Thus, methods for less
expensive cures for these polymers which produce
thermally and chemically stable crosslinked networks are
desirable.

U. S. Patents 4,281,092 and 4,394,489 and commonly
25 assigned U.S. Patent Application 08/197,516, filed
February 16, 1994, describe the preparation and/or
curing of nitrile containing perfluoroelastomers. The
curing is done in the presence of an organotin catalyst.
No mention is made of using a peroxide cure with these
30 polymers.

U.S. Patent 4,983,680 describes the peroxide
catalyzed curing (optionally with coagents) of a nitrile
containing perfluoroelastomer. No mention is made of
combining this cure with another cure.

SUMMARY OF THE INVENTION

This invention concerns a process for the curing of a perfluoroelastomer comprising:

- (a) confining to a specific shape a mixture
5 comprising:
 (i) a perfluoroelastomer containing a plurality of nitrile groups;
 (ii) a tin catalyst capable of catalyzing the crosslinking of said perfluoroelastomer through said
10 nitrile groups; and
 (iii) a peroxide capable of crosslinking said perfluoroelastomer and a coagent which is a diene or triene;
while heating said mixture at a first temperature
15 sufficient to decompose said peroxide;
 (b) removing said mixture from confinement;
and
 (c) heating said mixture at a second
20 temperature, which is higher than said first temperature, for a period of time sufficient to form crosslinks from said nitrile groups.

This invention also concerns a composition comprising:

- a perfluoroelastomer containing a plurality of
25 nitrile groups;
 about 0.1 to about 10 parts by weight per hundred parts of said perfluoroelastomer of a tin catalyst capable of catalyzing the crosslinking of said perfluoroelastomer through said nitrile groups;
30 about 0.1 to about 10 parts by weight per hundred parts of said perfluoroelastomer of a peroxide capable of curing said perfluoroelastomer; and
 about 0.1 to about 10 parts by weight per hundred parts of said perfluoroelastomer of a coagent
35 which is a diene or triene.

Also described herein is a process for the catalyzed crosslinking of a perfluoroelastomer containing a plurality of nitrile groups by heating said perfluoroelastomer in the presence of a catalyst capable of curing said perfluoroelastomer through said nitrile groups, wherein the improvement is the use of triphenyltin hydroxide as said catalyst.

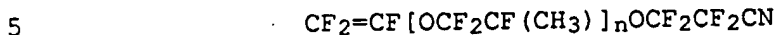
DETAILS OF THE INVENTION

The invention herein may be described as a dual cure system for a nitrile containing perfluoroelastomer. By a dual cure system is meant that it is believed that two (chemically) distinct types of cures take place, one caused by a peroxide and a coagent, and the other caused by a catalyzed reaction of nitrile groups.

The polymer used herein (in the curing process and in the composition to be cured) is a perfluoroelastomer containing a plurality of nitrile groups. By this is meant a perfluoroelastomer which contains a sufficient amount of nitrile groups which act as cure sites to crosslink the perfluoroelastomer. Usually, the nitrile groups are introduced by use of a nitrile containing cure site monomer, i.e., the nitrile groups are introduced into the polymer during polymerization. Suitable polymers are described in U.S. Patent 4,281,092, which is hereby included by reference. It is preferred if the perfluoroelastomer contains 0.1 to 2.5 mole percent of the nitrile containing cure site monomer.

Preferred perfluoroelastomers herein are copolymers of tetrafluoroethylene, a perfluoro(alkyl vinyl ether) and a nitrile containing cure site monomer. A preferred alkyl vinyl ether is perfluoro(methyl vinyl ether). An especially preferred perfluoroelastomer contains 53-79.9 mole percent tetrafluoroethylene, 20-46.9 mole percent perfluoro(methyl vinyl ether) and 0.1 to

2.5 mole percent nitrile containing cure site monomer. A preferred cure site monomer is a perfluorinated polyether having a nitrile group and a trifluorovinyl ether group. A more preferred cure site monomer is



wherein n is 1, 2, 3 or 4. An especially preferred cure site monomer is perfluoro(8-cyano-5-methyl-3,6-dioxa-1-octene).

The perfluoroelastomer is preferably made in emulsion systems using free radical initiation (see U.S. Patent 4,281,092, which is hereby included by reference). Chain transfer agents such as perfluoriodides, methylene iodide, and hydrocarbons can be used to control molecular weight to give lower viscosity polymers with better processing properties.

One of the cures of the dual cure employed herein uses a (organic) peroxide in combination with a coagent which is a diene or triene. For practical reasons in handling elastomeric materials, peroxides which decompose at 100°C or more, and which give relatively high energy free radicals are most suitable. Suitable peroxides are given in U.S. Patent 4,035,565, col. 5, lines 30 to 50, which patent is hereby included by reference. Useful peroxides include alpha, alpha'-bis-(t-butylperoxy)diisopropylbenzene and 2,5-bis(t-butylperoxy)-2,5-dimethylhexane. The peroxides may be used neat, but more commonly are used in some dilute form, such as on an inert carrier. Herein the amount of peroxide present is calculated based on pure peroxide. The peroxide is normally present in an amount in which it can effectively cure (crosslink) the perfluoroelastomer, typically about 0.1 to about 10 parts per hundred of perfluoroelastomer (all such parts herein are by weight). It is preferred if the amount of peroxide

used is about 0.3 to about 5 parts per hundred of the perfluoroelastomer.

A coagent is used in the peroxide cure. This coagent is a diene or a triene. Preferred coagents are triallylisocyanurate and triallylcyanurate. Other useful coagents are found in U.S. Patent 4,035,565, col. 6, lines 20-35, which is incorporated herein by reference. The coagent is normally present in an amount in which it can effectively cure (crosslink) the perfluoroelastomer, typically about 0.1 to about 10 part per hundred of perfluoroelastomer (all such parts herein are by weight). It is preferred if the amount of coagent used is about 0.3 to about 5 parts per hundred of the perfluoroelastomer.

In the peroxide portion of the dual cure the mixture containing the perfluoroelastomer is confined in a specific shape. What is meant by confined herein is that the mixture is held under a pressure sufficient to prevent the mixture from forming bubbles and voids, or distorting from the desired final part shape, presumably while the peroxide is forming crosslinks. This confinement will typically be in a mold, such as a compression or transfer mold.

The peroxide part of the cure is done at a first temperature, which is a temperature sufficiently high to cause thermal decomposition of the peroxide at a reasonable rate. The confined mixture is held at that first temperature for an amount of time sufficient to form enough crosslinks so that the part shape will be maintained, and no voids will form, when heated to the second temperature. This first temperature is typically about 150°C to about 220°C. Typical periods for this heating step are about 2 to about 60 minutes. Generally the shortest time at which sufficient crosslinking can be obtained will be used, since this maximizes

productivity of the equipment used, such as the molds and presses.

After this peroxide cured portion of the dual cure is done, the perfluoroelastomer may be removed from confinement. The other part of the dual cure system is believed to involve the nitrile groups present in the perfluoroelastomer, and the catalyst which is present in the mixture. Typically, the catalyst used is an organotin compound, see U.S. Patent 4,281,092 and U.S. Patent Application 08/197,516, filed February 16, 1994, both of which are hereby included by reference. Preferred catalysts are tetraphenyltin, and triphenyltin hydroxide. Triphenyltin hydroxide is especially preferred (in a dual cure or in a cure only involving the nitrile groups) since it cures nitrile containing perfluoroelastomers faster (see Example 4 and Comparative Example G).

This part of the dual cure is done at a second temperature which is high enough, and for an amount of time which is long enough, to effect cure (crosslinking) through the nitrile groups. Typically this will be a temperature of about 250°C to about 310°C, and a typical curing time is about 1 hr. to about 48 hr., preferably about 3 hr. to about 24 hr.

When the perfluoroelastomer is at the second temperature, or is being heated to the second temperature, it may be done in air, but it is preferred if it is done in an atmosphere of an inert gas such as nitrogen or argon.

It is believed that during the second part of the dual cure herein the nitrile groups, in the presence of a catalyst which can catalyze the reaction, trimerize to form s-triazine rings, which are the crosslinks. These crosslinks (whatever they are) are very thermally stable, even at temperatures of 275°C or above. By

contrast, crosslinks formed with peroxides are not as thermally stable, exhibiting instability at about 220°C. Therefore, for parts for high temperature use, "nitrile cures" are preferred.

5 However, nitrile cures are very slow, meaning that cure times in the mold are very long before the part may be demolded, since sufficient crosslinks must form to hold the part shape and prevent voids from forming. This makes the nitrile cure very expensive in terms of
10 labor and equipment productivity. On the other hand, a peroxide cure is much faster, but as mentioned above, is relatively thermally unstable. The dual cure system surprisingly combines the advantage of the peroxide cure, a relatively fast and economical cure, with the
15 advantage of the thermally stable crosslinks of the nitrile cure. In the Examples (numbered) and Comparative Examples (lettered) the following abbreviations are used:

8CNVE - perfluoro(8-cyano-5-methyl-3,6-dioxa-1-octene)

20 PMVE - perfluoro(methyl vinyl ether)

The following test methods are used in the Examples:

Mooney Scorch - ASTM D-1646

Oscillating Disc Rheometer (ODR) - ASTM D-2084

25 Tensile Properties - ASTM D-1708

Compression Set - ASTM D-1414

Polymers for the Examples and Comparative Examples

The polymers used in Examples 1, 2, and Comparative Examples A and B were made in an emulsion polymerization
30 at 85°C using ammonium persulfate as the initiator. The polymers contained 43.2% PMVE, 2.2% 8CNVE (the remainder tetrafluoroethylene) and had an inherent viscosity of 0.51. The polymer for Example 3 was similarly made, except I(CH₂)₄I was used for chain transfer. This
35 polymer contained 45.5% PMVE, 2.3% 8CNVE and 0.05%

iodine, and had an inherent viscosity of 0.43. The polymers for Comparative Examples were made in a similar way, except those for C and D were not made with an iodo chain transfer agent.

- 5 The compounds were made on a rubber mill and parts were molded on a press. In all these examples triphenyltin hydroxide (TPT-OH) was used as the catalyst, Luperco® (available from ATO Chemie, 50% active ingredient) 101XL [2,5-bis-(t-butylperoxy)-2,5-
- 10 dimethylhexane] as the peroxide and triallyl isocyanurate (TAIC) as the coagent. In Table 1 is shown examples of stocks with the dual cure system and with just the TPT-OH. Examples 2, 3, and B include the use of a plasticizer, Krytox® 16350 (available from
- 15 E. I. du Pont de Nemours and Company, Wilmington, DE).

TABLE 1
Cured Properties of
Perfluoroelastomer - Dual Cure System

	1	2	A	B	3
<u>Compound</u>					
Polymer	100	100	100	100	100
MT Black	30	30	30	30	30
TPT-OH	2	2	2	2	2
Luperco® 101XL	1	1	--	--	1
TAIC	1	1	--	--	1
Krytox® 16350	--	12	--	12	10
<u>Properties</u>					
Mooney Scorch 121°C No rise after 30 min. ODR 177°C/3° arc	64	59	55	53	66
ML, N.m	1.75	1.35	1.1	0.9	1.3
ts2, mins.	2	2.5	>5	>5	1.2
MH (30 min.), N.m	5.1	3.8	3.3	2.2	4.5
Mh-ML, N.m	3.35	2.45	2.2	1.4	3.2

Tensile Properties (O-Rings)

M50, MPa	4.98	2.71	2.88	1.74	2.67
M100, MPa	7.03	6.58	7.90	4.01	7.13
Tb, MPa	12.4	12.0	13.8	8.48	11.3
Eb, %	107	155	142	175	133
Comp. Set 204°C/70 h					
O-rings	15	23	19	26	23
After heat aging at 275°C for:					
3 days	20	21	18	22	25
7 days	23	28	18	26	26
14 days	24	26	20	24	30

The press cures for 1, 2 and 3 samples were at 177°C/15 min.

The press cures for A and B were done at 200°C/30 min.

All samples were post cured at 305°C for 42 h under an atmosphere of nitrogen.

The O-rings were heat aged in an air oven for the designated time and tested for comp. set at 204°C/70 h.

In another series of Comparative Examples polymers were cured either by a peroxide cure or just by tin catalysis, and there was a distinct difference in the properties between the two systems. The results are shown in Table 2.

TABLE 2

Physical Properties of Perfluoroelastomers
Cured by Peroxides and by Tetraphenyl Tin

Raw Polymer

PMVE wt %	43.70	43.00
8CNVE wt %	2.2	2.1
Inh. Visc.	0.60	0.46
Mooney at 121°C	134	52
Iodine wt %	0	0.14

Example	C	D	E	F
	<u>TPT Cure</u>	<u>Peroxide</u>	<u>TPT Cure</u>	<u>Peroxide</u>
Compound				
Polymer	100	100	100	100
MT Black	15	15	15	15
TPT	2	--	2	--
Luperco® 101XL	--	5	--	5
TAIC	--	3	--	3
ODR				
ML, N.m	2.1 (190°C)	2.1 (177°C)	1.0 (190°C)	1.4 (177°C)
Ts2, min.	>5	2.5	>5	2.0
MH (15 min.), N.m	2.7	4.6	1.5	4.8
MH-ML, N.m	0.6	2.5	0.5	3.4
<u>Tensile Properties</u>				
M100, MPa	4.13	7.23	3.45	10.7
Tb, MPa	14.1	13.8	13.1	14.5
Eb, %	160	140	180	120
Comp. Set 204°C/70 h				
Pellets	12	25	17	27
O-rings	16	30	28	29
After heat aging at 275°C for:				
O-rings				
3 days	19	55	28	60
7 days	21	60	26	57
14 days	20	60	28	63

The C and E samples were press cured at 200°C/30 min and the D and F at 175°C/15 min.

All samples were post-cured in an oven under nitrogen at 288°C for 46 hrs. before testing.

The samples were heat aged in an air oven for the designated time and the comp. sets were measured at 204°C/70 h.

EXAMPLE 4 AND COMPARATIVE EXAMPLE G

In a rubber mill were compounded, 1) a nitrile containing perfluoroelastomer (PMVE 44.0 wt %, 8CNVE 2.2 wt %, inh. visc. 0.55) made in an emulsion system using ammonium persulfate initiation at 85°C, 2) 10 phr MT black and 3) 1 phr triphenyltin hydroxide. From the compounded stock dumbbells and O-rings were molded in a press at 200°C/15 min. These parts were post-cured at 260°C/24 hr under an atmosphere of nitrogen before testing. The results are shown in Table 3 as Example 4.

A control (Comparative Example G), in which 2 parts of tetraphenyltin was used as the curing catalyst instead of triphenyltin hydroxide, was also done. All other conditions were the same as for Example 4.

Results are shown in Table 3.

ODR tests were also run (temperature of 177°C) and the results are shown in Figure 1. This Figure clearly indicates that the compound in which triphenyltin hydroxide was the catalyst cures (crosslinks) much faster than when tetraphenyltin is used as the catalyst.

TABLE 3

<u>Example</u>	<u>4</u>	<u>G</u>
<u>Tensiles</u>		
M100, MPa	5.95	5.97
M200, MPa	14.0	14.2
Tb, MPa	26.9	21.5
Eb, %	313	265
<u>Compression Set</u>		
204°C/70 h	21	24

What is claimed is:

1. A process for the curing of a perfluoroelastomer, comprising,

(a) confining to a specific shape a mixture,

5 comprising:

(i) a perfluoroelastomer containing a plurality of nitrile groups;

(ii) a tin catalyst capable of catalyzing the crosslinking of said perfluoroelastomer through said
10 nitrile groups; and

(iii) a peroxide capable of crosslinking said perfluoroelastomer and a coagent which is a diene or triene;

while heating said mixture at a first temperature
15 sufficient to decompose said peroxide;

(b) removing said mixture from confinement;

and

(c) heating said mixture at a second
temperature, which is higher than said first
20 temperature, for a period of time sufficient to form crosslinks from said nitrile groups.

2. The process as recited in Claim 1 wherein said perfluoroelastomer is a copolymer of a perfluoro(alkyl vinyl ether), tetrafluoroethylene, and a nitrile
25 containing cure site monomer.

3. The process as recited in Claim 1 wherein said perfluoroelastomer is a copolymer of 53-79.9 mole percent tetrafluoroethylene, 20-46.9 mole percent perfluoro(methyl vinyl ether), and 0.1 to 2.5 mole
30 percent perfluoro(8-cyano-5-methyl-3,6-dioxo-1-octene).

4. The process as recited in Claim 1 wherein said first temperature is about 150°C to about 220°C, said second temperature is about 250°C to about 320°C.

5. The process as recited in Claim 4 wherein
35 about 0.3 to about 5 parts by weight of said peroxide

per hundred parts of said perfluoroelastomer are present, about 0.3 to about 5 parts by weight of triallyl isocyanurate or triallyl cyanurate per hundred parts of said perfluoroelastomer are present, and about
5 0.3 to about 5 parts by weight of said catalyst per hundred parts of said perfluoroelastomer are present, said catalyst being an organotin compound.

6. The process as recited in Claim 3 wherein said first temperature is about 150°C to about 220°C, said
10 second temperature is about 250°C to about 320°C.

7. The process as recited in Claim 6 wherein about 0.3 to about 5 parts by weight of said peroxide per hundred parts of said perfluoroelastomer are present, about 0.3 to about 5 parts by weight of
15 triallyl isocyanurate or triallyl cyanurate per hundred parts of said perfluoroelastomer are present, and about 0.3 to about 5 parts by weight of said catalyst per hundred parts of said perfluoroelastomer are present, said catalyst being an organotin compound.

20 8. The process as recited in Claim 5 wherein said catalyst is tetraphenyltin or triphenyltin hydroxide.

9. The process as recited in Claim 7 wherein said catalyst is tetraphenyltin or triphenyltin hydroxide.

10. A composition comprising:
25 a perfluoroelastomer containing a plurality of nitrile groups;

about 0.1 to about 10 parts by weight per hundred parts of said perfluoroelastomer of a tin catalyst capable of catalyzing the crosslinking of said
30 perfluoroelastomer through said nitrile groups;

about 0.1 to about 10 parts by weight per hundred parts of said perfluoroelastomer of a peroxide capable of curing said perfluoroelastomer; and

about 0.1 to about 10 parts by weight per hundred parts of said perfluoroelastomer of a coagent which is a diene or triene.

11. The composition as recited in Claim 10 wherein
5 said perfluoroelastomer is a copolymer of a perfluoro-
(alkyl vinyl ether), tetrafluoroethylene, and a nitrile
containing cure site monomer.

12. The composition as recited in Claim 10 wherein
10 said perfluoroelastomer is a copolymer of 53-79.9 mole
percent tetrafluoroethylene, 20-46.9 mole percent
perfluoro(methyl vinyl ether), and 0.1 to 2.5 mole
percent perfluoro(8-cyano-5-methyl-3,6-dioxo-1-octene).

13. The composition as recited in Claim 10 about
15 0.3 to about 5 parts by weight of said peroxide per
100 parts of perfluoroelastomer are present, wherein
about 0.3 to about 5 parts by weight of triallyl
isocyanurate or triallyl cyanurate per hundred parts of
said perfluoroelastomer are present, and about 0.3 to
20 about 5 parts by weight of said catalyst per hundred
parts of said perfluoroelastomer are present, said
catalyst being an organotin compound.

14. The composition as recited in Claim 12 wherein
about 0.3 to about 5 parts by weight of said peroxide
per 100 parts of said perfluoroelastomer are present,
25 about 0.3 to about 5 parts by weight of triallyl
isocyanurate or triallyl cyanurate per hundred part of
said perfluoroelastomer are present and about 0.3 to
about 5 parts by weight of said catalyst per hundred
parts of said perfluoroelastomer are present, said
30 catalyst being an organotin compound.

15. The composition as recited in Claim 14 wherein
said catalyst is tetraphenyltin or triphenyltin
hydroxide.

16. A process for the catalyzed crosslinking of a
35 perfluoroelastomer containing a plurality of nitrile

groups by heating said perfluoroelastomer in the presence of a catalyst capable of curing said perfluoroelastomer through said nitrile groups, wherein the improvement is the use of triphenyltin hydroxide as said catalyst.

17. The process as recited in Claim 16 wherein said perfluoroelastomer is a copolymer of a perfluoro(alkyl vinyl ether), tetrafluoroethylene, and a nitrile containing cure site monomer.

18. The process as recited in Claim 16 wherein said perfluoroelastomer is a copolymer of 53-79.9 mole percent tetrafluoroethylene, 20-46.9 mole percent perfluoro(methyl vinyl ether), and 0.1 to 2.5 mole percent perfluoro(8-cyano-5-methyl-3,6-dioxo-1-octene).

INTERNATIONAL SEARCH REPORT

Inter national Application No
PCT/US 95/04698

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/14 C08K5/57 C08J3/24 C08F8/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K C08J C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 424 555 (DU PONT) 2 May 1991 cited in the application see page 2, line 50 - page 3, line 2; claims 1-4,6,7,14; examples A,1	1-3, 10-12
A	EP,A,0 011 853 (DU PONT) 11 June 1980 cited in the application see page 13, line 19 - line 27; claims 1-10; examples	1-3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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NL - 2280 HV Rijswijk
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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